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COMPOSITE MATERIAL OF THE CORUNDUM – ZIRCONIUM DIOXIDE – SINTERING ADDITIVE SYSTEM

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A composite material based on Al_2O_3 is developed, which contains partly stabilized ZrO_2 as the reinforcing component and a eutectic of the system $\text{CaO} - \text{ZnO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ as the sintering additive. The use of initial material in the form of aluminum oxide obtained from aluminum hydroxide makes it possible to synthesize a material with average bending strength of 530 MPa at the firing temperature of 1550°C.

Contemporary engineering calls for the development of new materials with a perfect structure and a high level of properties. This holds for polymers, glasses, ceramics, metals, and composites on their basis. Considering the field of ceramic materials, one can see that the most commonly used oxide materials are corundum and zirconium dioxide; moreover, the range of promising composites within the $\text{Al}_2\text{O}_3 - \text{ZrO}_2$ system encompasses virtually the entire series of compositions between aluminum oxide and zirconium dioxide [1].

However, the substantial sintering temperature of these materials has motivated a search for new technological solutions, since the earlier produced ceramics of this class have become noncompetitive.

Some researchers still attempt to find methods for achieving complete sintering of corundum ceramics at a temperature not higher than 1500°C [2]. However, certain techniques have now been developed controlling the sintering of such ceramics and bringing its sintering temperature down to 1350 – 1550°C. Modifiers that decrease the sintering temperature are eutectic additives in an amount no more than 5% (here and elsewhere mass content unless otherwise specified) [3, 4].

The application areas for the newly developed materials are quite diverse. They can be used in electronic engineering, as tap gaskets, thread carriers, insulators, wear-resistant milling bodies, and other purposes. However, the use of these materials in fields of engineering involving high mechanical loads (cutting tool, bearings, pump plungers, high pressure injectors, etc.) is rather limited.

In order to improve the physicomechanical characteristics of corundum ceramics, we have attempted to develop a

dispersion-strengthened composite based on Al_2O_3 containing both a strengthening component and a sintering(modifying) additive. A highly dispersed tetragonal solid solution based on ZrO_2 was chosen as the component increasing the mechanical strength of ceramics.

Since the range of ternary eutectic additives providing for a significant decrease in sintering temperature and the principles of their selection are known [4], we propose using eutectics of the four-component system $\text{CaO} - \text{ZnO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$. It should be noted that this additive is chosen for experiments based on the earlier used principles [4]. The considered system has several invariant points, including eutectics with melting temperatures of 1320 and 1200°C (hereafter named additives 1 and 2, respectively).

The initial components for producing eutectic additives were ZnO , $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, and amorphous SiO_2 of grade not lower than “chemically pure.” Mixtures of the estimated composition were loaded into a ball mill and milled by wet grinding.

The differential-thermal analysis of material mixtures indicates that the eutectic phases are completely synthesized at a temperature of 1000°C, which is also corroborated by the petrographic analysis of initial mixtures fired at temperatures of 900, 1000, and 1100°C. The initial powders after milling were subjected to synthesis at a temperature of 1000°C. The furnace heating rate was 3 K/min, and the exposure at the maximum firing temperatures was 3 h. The calcined materials were subjected to wet grinding under the same conditions as before the heat treatment.

To obtain partly stabilized ZrO_2 , we used the method of heterophase precipitation. The initial precursor salt (zirconium oxychloride crystal octahydrate) was dissolved in distilled water heated up to $100 \pm 5^\circ\text{C}$. The obtained solution was evaporated to a concentration equal to 0.9C (C is the salt

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solubility at the specified temperature). The concentration of the solution was controlled based on its density. The salt solution at a pressure of 1×10^4 Pa was sprayed by means of compressed nitrogen through a glass capillary of diameter 1.0 – 1.5 mm into a saturated ammonia solution whose temperature was minus 20°C. The resulting suspension was poured into a Buchner funnel and rinsed with distilled water up to pH \approx 6.0 in the filtrate. The precipitate was dried using acetone.

Yttrium chloride was added to zirconium hydroxide in the amount of 3 mol.% Y_2O_3 for stabilizing synthesized ZrO_2 . The prepared composition was mixed with acetone and milled for 3 min in a planetary mill.

According to DTA data, the synthesis of a tetragonal solid solution occurs at a temperature of 580°C. Therefore, the milled powder was calcined at 600°C. The furnace heating rate was 3 K/min, and the exposure at the maximum temperature was 3 h. The powder after synthesis was milled in the same conditions as before the heat treatment. The size of solid solution aggregates (measured by scanning electron microscopy) is 0.3 – 0.5 μ m; the aggregates consist of individual crystals of size 20 – 40 nm.

The initial alumina material was alumina GLMK milled by wet grinding for 24 h and aluminum oxide obtained from industrially produced aluminum hydroxide (Al_2O_3 -H).

Aluminum hydroxide was milled in a ball mill. Base magnesium carbonate was added into the mill before milling to modify aluminum oxide in the amount of 0.25% MgO. The $Al(OH)_3$ obtained after drying was heat-treated at a temperature of 1350°C with an exposure at the maximum temperature equal to 3 h. The heating rate was 3 K/min. The material after heat treatment was milled in a ball mill.

The initial powder was prepared by wet milling in a ball mill of compositions based on the alumina component containing 20% ZrO_2 and 4 or 5% sintering additive.

The temporary technological binder for semidry molding was 5% polyvinyl alcohol solution introduced in the amount of 20% of the batch weight. The molding powder was grated through a sieve and used to mold bar-shaped samples of size 40 \times 6 \times 6 mm, which were molded by bilateral uniaxial molding under a pressure of 100 MPa.

Firing was performed in air at the rate of 3 K/min in the temperature interval of 1500 – 1600°C with the exposure at the final temperature equal to 3 h.

The properties of ceramics based on alumina GLMK are listed in Table 1. Comparing additives with respect to their effect on sinterability of ceramics, it should be noted that, other terms being equal (equal firing temperatures, initial materials, and quantities of additives), the properties of the material with additive 2 are better than those of the ceramic with additive 1. The latter could be expected, since the melting temperature of additive 1 is significantly higher than that of additive 2.

Furthermore, increasing the quantity of the sintering additive from 4 to 5% causes an insignificant increase in water

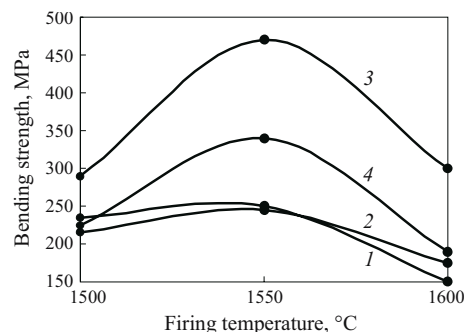


Fig. 1. Mechanical strength of ceramics based on alumina GLMK with additive 1 (1, 2) and 2 (3, 4) in the system $CaO - ZnO - Al_2O_3 - SiO_2$. The content of additives: 1, 3) 4%; 2, 4) 5%.

absorption. A probable reason for this phenomenon may be partial destabilization of the ZrO_2 -based tetragonal solid solution in the presence of SiO_2 , which is reported, for instance in [5]. This assumption is corroborated by the results of petrographic analysis. Thus, upon introducing 4% modifying additive in the initial composition, the quantity of monoclinic ZrO_2 in the sintered material is below 2%, whereas with 5% additive it is equal to 12 – 15%.

Using Al_2O_3 -H as initial material does not make the average density higher than similar compositions based on alumina GLMK.

The results of determining the mechanical strength of ceramics based on GLMK with the specified additives are given in Fig. 1. It can be seen that at the firing temperature of 1550°C the strength parameter reaches its maximum for all investigated types and quantities of sintering additives. The ceramic containing 4% additive 2 is stronger than the material obtained with 5% additive. The latter is presumably due to the tetragonal solid solution becoming destabilized as a consequence of introducing an excess amount of SiO_2 . Consequently, the use of this additive in an amount over 4% decreases the strength of material. It should be noted that the limiting quantity of this additive (converted to silica) that does not lead to destabilization is 1.73%.

TABLE 1

Firing temperature, °C	Properties of ceramics containing additive in amount of					
	4%			5%		
	linear shrinkage, %	mean density, g/cm ³	water absorption, %	linear shrinkage, %	mean density, g/cm ³	water absorption, %
<i>Additive 1</i>						
1500	14.2	3.91	0.80	15.1	3.89	0.8
1550	15.6	4.06	0.02	15.3	4.04	0.3
1600	16.6	4.08	0.02	16.6	4.05	0.2
<i>Additive 2</i>						
1500	14.9	3.96	0.7	15.1	3.98	0.6
1550	16.1	4.03	0.0	16.1	4.04	0.1
1600	16.2	4.04	0.0	16.6	4.04	0.1

The introduction of additive 1 in all cases does not produce a high-strength materials, since, even with 4% content of additive 1 in the batch, the amount of SiO_2 in the material is equal to 1.95%, which exceeds the above specified limiting value.

Thus, the use of 4% additive 2 makes it possible to synthesize materials with average bending strength equal to 470 MPa at the firing temperature of 1550°C. Using alumina produced from aluminum hydroxide in combination with 4% additive 2 and 20% partly stabilized ZrO_2 make it possible to obtain a material with a bending strength of 530 MPa at the firing temperature of 1550°C. Some samples in this case reach the strength of 560 MPa.

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